Refinement

Refinement on F
$R = 0.028$
$wR = 0.027$
$S = 1.69$
1040 reflections
140 parameters
Only coordinates of H atoms refined
$w = 4F_o^2/\sigma^2(F_o^2)$
$(\Delta/\sigma)_{\max} = 0.01$
$\Delta\rho_{\max} = 0.25$ e Å^{-3}
$\Delta\rho_{\min} = -0.34$ e Å^{-3}
Extinction correction: Zachariasen (1968) Type II, Gaussian isotropic
Extinction coefficient: 0.00000268 (19)
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Table 4. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2) for (II)*

$$U_{\rm eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$U_{\rm eq}$
Mn(1)	1	0	1	0.0192 (2)
S(1)	0.7300 (1)	0.1686 (1)	1.38918 (4)	0.0222 (2)
O(1)	0.8667 (4)	0.0174 (3)	1.4227 (1)	0.0351 (7)
O(2)	0.8204 (4)	0.3527 (3)	1.4125 (1)	0.0302 (7)
O(3)	0.4905 (4)	0.1483 (4)	1.3989 (1)	0.0400 (8)
O(4)	1.2762 (4)	0.2062 (3)	1.0070 (1)	0.0267 (7)
N(1)	0.7995 (5)	0.1922 (4)	1.0743 (1)	0.0235 (8)
C(1)	0.7554 (5)	0.1623 (4)	1.2964 (2)	0.0186 (8)
C(2)	0.9563 (5)	0.2220 (4)	1.2698 (2)	0.0229 (9)
C(3)	0.9710 (6)	0.2264 (5)	1.1966 (2)	0.0232 (9)
C(4)	0.7869 (5)	0.1750 (4)	1.1504 (2)	0.0196 (8)
C(5)	0.5915 (5)	0.1076 (5)	1.1772 (2)	0.0225 (9)
C(6)	0.5764 (5)	0.1015 (4)	1.2503 (2)	0.0228 (9)
H(1)	0.670 (5)	0.182 (5)	1.056 (2)	
H(2)	0.861 (5)	0.306 (4)	1.064 (2)	
H(3)	1.075 (5)	0.271 (4)	1.301 (2)	
H(4)	1.094 (5)	0.272 (4)	1.179 (2)	
H(5)	0.471 (5)	0.071 (4)	1.145 (2)	
H(6)	0.445 (5)	0.057 (4)	1.268 (2)	
H(7)	1.247 (5)	0.305 (4)	1.027 (2)	
H(8)	1.346 (5)	0.249 (4)	0.973 (2)	

Table 5. *Selected geometric parameters (Å, °) for (II)*

Mn(1)—O(2^{i})	2.152 (2)	S(1)—O(2)	1.466 (2)
Mn(1)—O(4)	2.189 (2)	S(1)—O(3)	1.449 (2)
Mn(1)—N(1)	2.343 (3)	S(1)—C(1)	1.762 (3)
S(1)—O(1)	1.456 (2)	N(1)—C(4)	1.444 (4)
O(2^{i})—Mn(1)—O(4)	92.22 (9)	O(2)—S(1)—O(3)	112.7 (1)
O(2^{ii})—Mn(1)—N(1)	94.02 (9)	O(2)—S(1)—C(1)	105.1 (1)
O(4)—Mn(1)—N(1^{iii})	90.8 (1)	O(3)—S(1)—C(1)	106.7 (1)
O(1)—S(1)—O(2)	110.7 (1)	Mn(1)—N(1)—C(4)	127.7 (2)
O(1)—S(1)—O(3)	112.6 (1)	Mn(1)—O(2^{i})—S(1^{i})	143.8 (1)
O(1)—S(1)—C(1)	108.6 (1)		

Symmetry codes: (i) $x, \frac{1}{2} - y, z - \frac{1}{2}$; (ii) $2 - x, y - \frac{1}{2}, \frac{5}{2} - z$; (iii) $2 - x, -y, 2 - z$.

Table 6. *Hydrogen-bonding geometry (Å, °) for (II)*

D—H···A	D—H	H···A	D···A	D—H···A
N(1)—H(2)···O(1^{i})	0.91 (3)	2.20 (3)	3.035 (3)	152 (3)
O(4)—H(7)···O(1^{i})	0.82 (3)	1.93 (3)	2.744 (3)	171 (3)
O(4)—H(8)···O(3^{ii})	0.85 (3)	1.84 (3)	2.688 (3)	177 (3)

Symmetry codes: (i) $2 - x, \frac{1}{2} + y, \frac{5}{2} - z$; (ii) $1 + x, \frac{1}{2} - y, z - \frac{1}{2}$.

All H atoms were located on difference electron density maps and their positions refined with fixed isotropic B values equal to 1.2 times those of the attached atoms at the time of their inclusion. Bond distances: (I) N—H 0.82 (3)–0.83 (3), C—H 0.86 (3)–0.93 (3) Å; (II) N—H 0.81 (3)–0.91 (3), C—H 0.88 (3)–0.95 (3) Å.

For both compounds, data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1988); cell refinement: *MSC/AFC Diffractometer Control Software*; data reduction: *TEXSAN* (Molecular Structure Corporation, 1991); program(s) used to solve structures: *MITHRIL* (Gilmore, 1983); program(s) used to refine structures: *TEXSAN*; software used to prepare material for publication: *TEXSAN*.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry, including intermolecular distances involving both H and non-H atoms, have been deposited with the IUCr (Reference: BK1192). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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A Copper(II) Complex of a Macrocyclic Schiff Base Ligand with a Polyether Bridge

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(Received 20 December 1995; accepted 29 January 1996)

Abstract

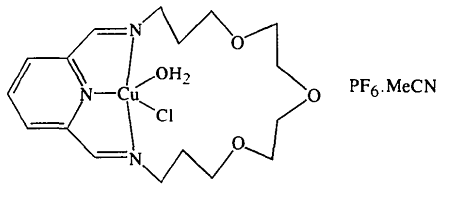
In the structure of aquachloro[7,10,13-trioxa-3,17,23-triazabicyclo[17.3.1]tricosa-1(23),2,17,19,21-pentaene-N,N',N'']copper(II) hexafluorophosphate acetonitrile solvate, the Cu$^{\rm II}$ ion is pentacoordinate with square-pyramidal coordination geometry, with a relatively long axial bond to water [2.244 (5) Å] and with the shortest

Acta Crystallographica Section C
ISSN 0108-2701 ©1996

Cu—N bond being to the pyridine N atom. The water molecule is also hydrogen bonded to two O atoms of the ligand. The complex is folded about the N—Cu—N axis, the polyether chain being nearly planar and making an angle of about 135° with the pyridine ring.

Comment

The synthesis of multidentate macrocyclic ligands derived from 2,6-dicarbonylpyridines and aliphatic diamines *via* the metal ion template effect has been known for some time (Curry & Busch, 1964). In the presence of the large lead(II) ion, the Schiff base condensation of 2,6-pyridinedicarboxaldehyde with 1,11-diamino-3,6,9-trioxaundecane gave a hexadentate macrocyclic ligand with each donor atom coordinated to the lead(II) ion (Fenton, Cook & Nowell, 1977). We report here the properties of the smaller copper(II) ion, both as the templating metal and in relation to the bonding to a related macrocycle, as the title compound (I).



(I)

The ring closure reaction between the aldehyde and the diamine proved to be straightforward, providing the copper complex in good yield. The ligand macrocycle is coordinated only through the N atoms, with the copper coordination completed by a Cl^- ion and a water molecule. Indeed, incorporation of the water molecule is clearly favoured; as well as being bound to the copper, it is hydrogen-bonded to two of the macrocyclic O atoms [O···O 2.706 (5) Å; O···O···O 117.3 (5)°]. The overall geometry is close to square-pyramidal with the O atom in an axial position (Fig. 1*a*). A search of the Cambridge Structural Database (Allen *et al.*, 1991) indicates that this coordination group is rare though not unknown (31 examples), though none of the examples included the 2,6-dimethyleneaminopyridine unit. The Cu—N bond lengths have typical values, with the bond to the pyridine N atom 0.151 (5) Å shorter than the other Cu—N bonds. The equatorial Cu—Cl bond [2.217 (2) Å] has the expected value (*cf.* 2.19 Å in a similar Cu dioxime; Vasilevsky *et al.*, 1989). The length of the axial Cu—O bond [2.244 (5) Å] indicates that it is considerably weaker than the equatorial bonds, as also observed in related complexes (*e.g.* Cu—Cl 2.60 Å in the dioxime complex mentioned above).

For the complex as a whole, the polyether chain is nearly planar, making an angle of about 135° with the pyridine ring (Fig. 1*b*). The bending is mediated by the *gauche* conformation of the polyether chain and in particular the C7—C8 bond. A similar folded 'hairpin' geometry is found in a complex containing copper coordinated to two pyridine and two amino N atoms, though in this example the chain N atoms are reduced (Fronczek, Mamo & Pappalardo, 1989).

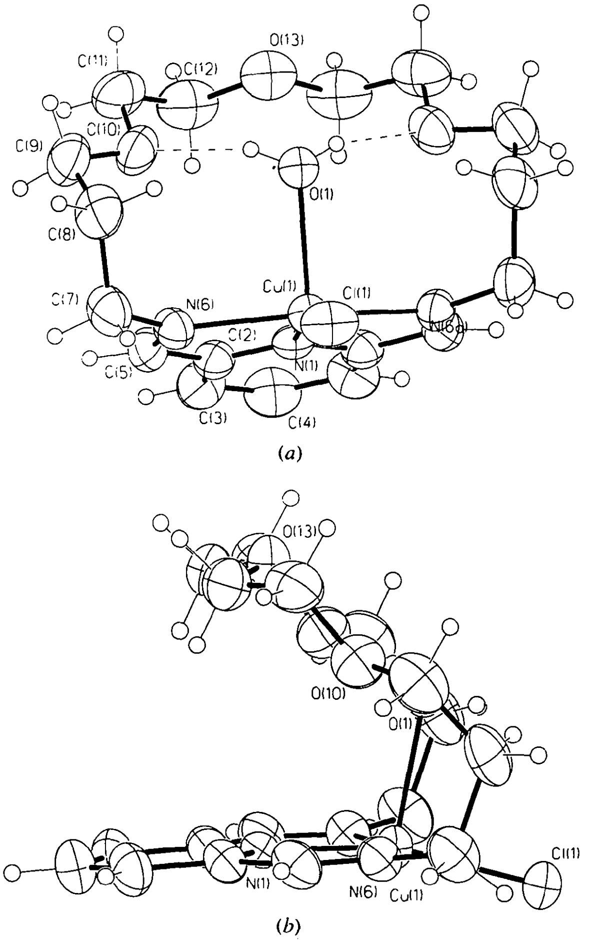


Fig. 1. (*a*) View of the cation showing the atomic numbering. (*b*) Side view of the cation showing the inclined planes of the pyridine and polyether sections. Displacement ellipsoids are drawn at the 50% probability level.

Experimental

$CuCl_2.2H_2O$ (0.514 g, 3.02 mmol) and 2,6-pyridinedicarboxaldehyde (0.407 g, 3.01 mmol) were dissolved in 200 ml of methanol with stirring. A small amount of concentrated hydrochloric acid was added followed by slow addition of 1,13-diamino-4,7,10-trioxatridecane (0.665 g, 3.02 mmol) in 30 ml of methanol at a rate of about one drop every two seconds. After addition of the diamine, solvent volume was reduced to about 50 ml by rotary evaporation and excess NH_4PF_6 in methanol was added, giving a precipitate upon further rotary evaporation of the solvent. The crude product, a light-green powder, was recrystallized by slow evaporation of a 1:1 mixture of acetonitrile/ethanol to yield emerald green crystals.

Crystal data

$[CuCl(H_2O)(C_{17}H_{25}N_3O_3)]$-
$PF_6.CH_3CN$
$M_r = 581.38$
Orthorhombic
Pbam
$a = 26.618\,(9)$ Å
$b = 8.950\,(4)$ Å
$c = 10.889\,(4)$ Å
$V = 2594.1\,(17)$ Å^3
$Z = 4$
$D_x = 1.489$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 23 reflections
$\theta = 13$–$15°$
$\mu = 1.076$ mm^{-1}
$T = 293\,(2)$ K
Plates
$0.62 \times 0.22 \times 0.19$ mm
Green

Data collection

Siemens *R*3*m* four circle diffractometer
ω–2θ scans
Absorption correction: analytical (*ABSPSI*; Alcock & Marks, 1994)
$T_{min} = 0.78$, $T_{max} = 0.84$
3139 measured reflections
2431 independent reflections
1847 observed reflections [$I > 2\sigma(I)$]

$R_{int} = 0.0315$
$\theta_{max} = 25.06°$
$h = -1 \rightarrow 31$
$k = -1 \rightarrow 10$
$l = -1 \rightarrow 12$
3 standard reflections
monitored every 200 reflections
intensity decay: 2%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.0584$
$wR(F^2) = 0.1768$
$S = 1.016$
2429 reflections
190 parameters
H atoms riding
$w = 1/[\sigma^2(F_o^2) + (0.1002P)^2 + 5.0808P]$
where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max} = -0.471$
$\Delta\rho_{max} = 0.774$ e Å^{-3}
$\Delta\rho_{min} = -0.543$ e Å^{-3}
Extinction correction: none
Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)

Table 1. *Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters* (Å^2)

$$U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}/U_{iso}
Cu1	0.07268 (3)	0.00673 (8)	0	0.0386 (3)
Cl1	0.02604 (7)	−0.1984 (2)	0	0.0567 (5)
O1	0.1456 (2)	−0.1190 (5)	0	0.0409 (10)
N1	0.0952 (2)	0.2137 (5)	0	0.0357 (11)
C2	0.1007 (2)	0.2835 (5)	0.1060 (4)	0.0420 (10)
C3	0.1137 (2)	0.4341 (5)	0.1093 (5)	0.0556 (13)
C4	0.1196 (3)	0.5073 (8)	0	0.062 (2)
C5	0.0914 (2)	0.1850 (5)	0.2116 (5)	0.0491 (12)
N6	0.07859 (14)	0.0527 (4)	0.1883 (4)	0.0430 (9)
C7	0.0727 (2)	−0.0529 (7)	0.2905 (5)	0.0603 (14)
C8	0.1180 (2)	−0.1573 (6)	0.2989 (5)	0.0628 (15)
C9	0.1683 (2)	−0.0854 (7)	0.3213 (5)	0.068 (2)
O10	0.18504 (14)	−0.0141 (4)	0.2122 (3)	0.0574 (9)
C11	0.2348 (2)	0.0462 (7)	0.2179 (6)	0.069 (2)
C12	0.2428 (2)	0.1394 (6)	0.1093 (6)	0.070 (2)
O13	0.2416 (2)	0.0529 (6)	0	0.0602 (14)
P1	0.16448 (8)	0.4116 (2)	1/2	0.0558 (5)
F1	0.1297 (3)	0.2672 (8)	1/2	0.122 (3)
F21†	0.1928 (5)	0.5595 (10)	1/2	0.146 (5)
F31†	0.1835 (3)	0.3341 (10)	0.3791 (9)	0.165 (5)
F41†	0.1275 (6)	0.4899 (9)	0.4124 (12)	0.220 (6)
F22‡	0.2221 (9)	0.460 (4)	1/2	0.080 (8)
F32‡	0.2161 (5)	0.3410 (17)	0.4677 (15)	0.073 (6)
F42‡	0.1586 (7)	0.450 (2)	0.3704 (15)	0.065 (5)
O002§	0	0.245 (2)	1/2	0.098 (4)
O003§	0.0 (6)	−0.331 (2)	0.4163 (15)	0.164 (6)
O004¶	0.0047 (9)	−0.454 (2)	0.3073 (18)	0.093 (6)

† Occupancy 0.78 (1). ‡ Occupancy 0.22 (1); U_{iso}. § Occupancy 0.25; U_{iso}. ¶ Occupancy 0.5; U_{iso}.

Table 2. *Selected geometric parameters (Å, °)*

Cu1—N1	1.947 (5)	Cu1—Cl1	2.217 (2)
Cu1—N6	2.098 (4)	Cu1—O1	2.244 (5)
N1—Cu1—N6	77.89 (11)	N1—Cu1—O1	102.1 (2)
N6—Cu1—N6^i	155.8 (2)	N6—Cu1—O1	91.91 (11)
N1—Cu1—Cl1	163.9 (2)	Cl1—Cu1—O1	93.96 (13)
N6—Cu1—Cl1	101.80 (11)		

Symmetry code: (i) $x, y, -z$.

The structure was solved by direct methods using *SHELXTL-Plus* (Sheldrick, 1991), revealing the cation and $[PF_6]^-$ anion both lying on special positions with mirror symmetry. The cation is well determined, but the anion is highly disordered and was refined with one full and six partial (refined) occupancy F atoms. All P—F distances were restrained to be equal. A disordered solvent molecule (presumably acetonitrile at about 0.5 occupancy) lying on a mirror plane was treated as one 0.5 occupancy and two 0.25 occupancy O atoms. H atoms were added at calculated positions and refined using a riding model. The unique proton attached to the coordinated H_2O was located from a difference Fourier synthesis and refined with the O—H distance restrained to 0.90 (3) Å. Anisotropic displacement parameters were used for all non-H atoms apart from the low-occupancy fluorine and solvent atoms; H atoms were given isotropic displacement parameters equal to 0.08 e Å^{-2}. *SHELXL*93 (Sheldrick, 1993) was used for refinement.

We thank NATO for travel support for the Warwick–Kansas collaboration. ALV thanks the Madison and Lila Self Graduate Fellowship for financial support. We wish to acknowledge the use of the EPSRC's Chemical Database Service at Daresbury.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: AB1348). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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